EFFECT OF CO_2 ON PRODUCTION OF JATROPHA OIL METHYL ESTER VIA SUB/SUPERCRITICAL METHANOL

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ABSTRACT

This research focused on effect of co-solvent towards production of biodiesel via sub/supercritical methanol. The objective of this research is to study the effect of CO_2 as co-solvent in production of Jatropha Oil Methyl Ester at sub/Supercritical of methanol and to optimize operating parameters such as reaction temperature, CO_2 volume and the ratio of methanol/oil. The reaction has been carried out in the absence of catalyst due to the easier purification process. The raw materials used in this study are refined jatropha oil, high grade methanol (solvent) and CO_2 (co-solvent). It is believed that addition of co-solvent with lower critical point will reduce the severity of reaction temperature and pressure. Jatropha oil, methanol and CO_2 were charged into the supercritical reactor with appropriate mole ratio. The mixture is then heated up to desired reaction temperature. The reaction pressure was recorded and the reactor is cooling down until room temperature. The product is then removed and proceeds for purification. The product sample is analyzed to determine the yield percentage of methyl ester using gas chromatography. The duration for reaction was fixed at 5 minutes. The reaction temperature was varied at 160^{o}C to 300^{o}C. CO_2 is added into reaction system and act as co-solvent in order to decrease the pressure. The amount of CO_2 added is measured in terms of volumes, which are at 0.018 m^3, 0.055 m^3 and 0.092 m^3, respectively. Result shows that, addition of CO_2 in the reaction system manage to decrease the reaction pressure. The best volume of CO_2 addition obtained from this study was 0.018 m^3 with reaction pressure 15.1 MPa and yields 85.45 w/w% of jatropha oil methyl ester (JOME) at reaction temperature of 300^{o}C. This study shows that, the addition of CO_2 as co-solvent is a promising method to reduce the reaction pressure and acceptable for future studies.

ABSTRAK

Fokus kajian ini ialah terhadap kesan larutan sampingan ke atas penghasilan biodiesel pada bawah tahap genting dan atas tahap genting methanol. Objektif penyelidikan ini adalah untuk mengkaji kesan larutan sampingan dalam penghasilan Minyak Jatropha Metil Ester (JOME) pada bawah tahap genting dan atas tahap genting methanol dan tahap optima pemboleh ubah seperti suhu tindak balas, isipadu karbon dioksida dan nisbah mol minyak/alkohol. Tindak balas telah dijalankan tanpa kehadiran pemangkin untuk memudahkan proses penulenan . Bahan mentah yang digunakan dalam kajian ini adalah minyak jatropha, metanol berkualiti tinggi sebagai pelarut, dan karbon dioksida sebagai pelarut sampingan. Dipercayai bahawa dengan penambahan pelarut sampingan yang mempunyai tahap genting yang lebih rendah dapat mengurangkan keparahan suhu dan tekanan tindak balas. Minyak jatropha, metanol dan karbon dioksida dimasukkan ke dalam penindak balas mengikut nisbah yang di tetapkan. Campuran itu tadi di panaskan sehingga mencapai suhu tindak balas yang di kehendaki dan apabila tindak balas lengkap, tekanan tindak balas direkodkan serta di sejukkan ke suhu bilik. Produk di keluarkan untuk proses penulenan dan contoh produk di analisis menggunakan kromatografi gas untuk menentukan jumlah peratusan metil ester. Jangka masa tindak balas di tetapkan pada 5 minit. Suhu tindak balas telah di variasi kan dari $160^{O}C$ kepada $300^{O}C$. Karbon dioksida telah di masukkan ke dalam sistem dan bertindak sebagai larutan sampingan untuk mengurangkan tekanan. Jumlah karbon dioksida yang di masukkan di sukat dalam unit isipadu, iaitu pada 0.018 m^3, 0.055 m^3 dan 0.092 m^3, masing- masing. Berdasarkan keputusan yang di perolehi, penambahan karbon dioksida ke dalam tindak balas dapat mengurangkan tekanan semasa tindak balas. Isipadu terbaik yang di perolehi berdasarkan kajian ialah ialah 0.018 m^3 dengan tekanan dalam tindak balas 15.1MPa dan hasil JOME ialah 85.45 w/w % pada suhu tindak balas $300^{o}C$. Kajian ini menunjukkan, penambahan larutan sampingan adalah kaedah yang menjanjikan penurunan tekanan tindak balas dan boleh di guna pakai untuk kajian pada masa hadapan.

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ASTM	American Society for Testing and Materials
EPA	Environmental Protection Agency
FAME	Fatty Acid Methyl Ester
GL	Glycerin
SCM	Supercritical Methanol
T_{CA}	Critical Temperature of species A
T_{CB}	Critical Temperature of species B
TG	Triglyceride

CHAPTER 1

INTRODUCTION

1.1 Background of Study

A supercritical condition is a condition when a substance at temperature and pressure above its critical point. The supercritical fluid at supercritical condition can diffuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned". Carbon dioxide and water are the most commonly used as supercritical fluids (Supercritical fluid 2009).

In addition, there is no surface tension in a supercritical condition, as there is no liquid or gas phase boundary. By changing the pressure and temperature of the fluid, the properties can be “tuned” to be more liquid- or more gas-like. One of the most important properties is the solubility of material in the fluid. Solubility in a supercritical fluid tends to increase with density of the fluid (at constant temperature). Since density increases with pressure, solubility tends to increase with pressure. The relationship with temperature is a little more complicated. At constant density, solubility will increase with temperature. However, close to the critical point, the density can drop sharply with a slight increase in

temperature. Therefore, close to the critical temperature, solubility often drops with increasing temperature, and then rises again (Supercritical fluid 2009).

All supercritical fluids are completely miscible with each other so for a mixture a single phase can be guaranteed if the critical point of the mixture is exceeded. The critical point of a binary mixture can be estimated as the arithmetic mean of the critical temperatures and pressures of the two components (Supercritical Fluid 2009)

$T_{C(mix)}$ = (mole fraction A) x T_{CA} + (mole fraction B) x T_{CB}. (1)

For greater accuracy, the critical point can be calculated using equations of state, such as the Peng Robinson, or group contribution methods. Other properties, such as density, can also be calculated using equations of state. Any commercialization of a process that uses supercritical condition must involve a cost analysis that should indicate that the advantages in the new process offset the penalty of high pressure operations. A variety of supercritical condition processes have been commercialized (Supercritical Fluid 2009).

Many other processes have been investigated on a lab or pilot plant scale and have the potential to be scaled up in the near future. Supercritical condition widely used in supercritical fluid chromatography, fractionation, reaction, applications in the material and polymer industry, food applications, pharmaceutical application and environmental application .Another application of fluid highlighted in this research is the transesterification. Transesterification is one of the important processes in the production of biodiesel.

1.2 Problem Statement

Supercritical methanol is believed to solve problems associated with the two phase nature of normal methanol/oil mixtures in transesterification reaction by forming a single phase as a result of the lower value of the dielectric constant of methanol in the supercritical state. However, methanol/oil are alone in the production required temperatures of 350-400^{o}C and pressure of 45-65MPa, which are not viable in practice in industry (Cao et al.)

The purpose of this research is to study the effect of CO2 at different volume in production of methyl ester using lab scale high pressure reactor (batch mode). It is believed that, with CO2 as co-solvent in the reaction system, there was a significant decrease in the severity of the conditions required for supercritical reaction (Cao et al.)

1.3 Objectives of Research

The objectives of this project are:

- To study the effect of CO_2 on sub/supercritical methanol.
- To optimize operating parameters such as reaction temperature, CO_2 volume and the ratio of methanol/oil

1.4 Scope of Research

This research is conducted to study the effect of co-solvent added in the production of Jatropha Oil Methyl Ester at subcritical and supercritical condition. In order to reach subcritical and supercritical condition in the process, the reaction temperature is fixed at range of 160^{o}C to 300^{o}C .The significant of the range is due to the sub/supercritical point of methanol as solvent.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Transesterification of triglycerides are in oils is not a new process. Scientists E. Duffy and J. Patrick conducted it as early as 1853. The name ‘biodiesel’ has been given to transesterified vegetable oil to describe its use as a diesel fuel (Demirbas 2005).

Vegetable oils have not been accepted as a diesel engine fuel based on two reasons. They are more expensive than petroleum fuels and they are too viscous to be atomized efficiently in a diesel engine. With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for diesel engines. However, a need exists to find away to reduce their viscosity. Conversion of oil to its corresponding fatty ester appears to be the most promising solution to the high viscosity problem. The molecular weight is reduced to almost one third its value by esterification with subsequent marked reduction in viscosity (S. Hawash,2009)

2.2 Biodiesel

Biodiesel is the name of a clean burning alternative fuel, produced from domestic, renewable resources. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. Biodiesel is produced from any fat or oil such as soybean oil, through a refinery process called transesterification. This process is a reaction of the oil with an alcohol to remove the glycerin, which is a by-product of biodiesel production (Board, 2010).

Fuel-grade biodiesel must be produced to strict industry specifications of American Society for Testing and Materials (ASTM D6751) in order to insure proper performance. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conform to ASTM D6751 specifications for use in diesel engines. The National Biodiesel Board has released the following production volume estimates for the US (Board, 2010)

Table 2.1: Production of biodiesel in US

Year	Production of biodiesel, million gallons
2008	700
2007	450
2006	250
2005	75
2004	25
2003	20
2002	15

Sources: National Biodiesel Board 2010

It is clearly shows that the demand for biodiesel is increasing in US. However, this phenomenon also happens to other country all over the world. Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the Clean Air Act. The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter compared to emissions from diesel fuel. In addition, the exhaust emissions of sulfur oxides and sulfates (major components of acid rain) from biodiesel are essentially eliminated compared to diesel (Board, 2010).

Of the major exhaust pollutants, both unburned hydrocarbons and nitrogen oxides are ozone or smog forming precursors. The use of biodiesel results in a substantial reduction of unburned hydrocarbons. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods used. Based on engine testing, using the most stringent emissions testing protocols required by Environmental Protection Agency (EPA) for certification of fuels or fuel additives in the US, the overall ozone forming potential of the speciated hydrocarbon emissions from biodiesel was nearly 50 percent less than that measured for diesel fuel (Board, 2010).

2.3 Sources of Biodiesel

Vegetable oils and animal fat are two common feedstock used for biodiesel. However, vegetable oils are mostly used as the feedstock of biodiesel due to it is renewable sources such as soybean oil, corn oil, palm oil, jatropha oil, algae, cooking oil, seaweed, sunflower and sugarcane. However, the most popular vegetable oils for biodiesel feedstock are palm oil and algae.

2.3.1 Biodiesel from Algae

Algae have emerged as one of the most promising sources for biodiesel production. The current oil crises and fast depleting fossil oil reserves have made it more imperative for organizations and countries to invest more time and efforts into research on suitable renewable feedstock such as algae. An alga (singular alga) is a term that encompasses many different groups of living organisms. Algae capture light energy through photosynthesis and convert inorganic substances into simple sugars using the captured energy (Castoroil 2006).

Algae are usually found in damp places or bodies of water and thus are common in terrestrial as well as aquatic environments. However, terrestrial algae are usually rather inconspicuous and far more common in moist, tropical regions than dry ones, because algae lack vascular tissues and other adaptions to live on land. As mentioned above, algae grow in almost every habitat in every part of the world (Castoroil 2006). However, the production of biodiesel from algae is not practical for industry in Malaysia as the weather here is not constantly moist. Thus, algae are not a suitable feedstock for biodiesel in dry country such as in Malaysia.

2.3.2 Biodiesel from Palm Oil

Palm oil and palm kernel oil are composed of fatty acids, esterified with glycerol just like any ordinary fat. Both are high in saturated fatty acids, about 50% and 80%, respectively. The oil palm gives its name to the 16-carbon saturated fatty acid palmitic acid found in palm oil; monounsaturated oleic acid is also a constituent of palm oil while palm kernel oil contains mainly lauric acid (Palm Oil 2010).

Palm is also used to make biodiesel, as either a simply-processed palm oil mixed with petro diesel, or processed through transesterification to create a palm oil methyl ester blend, which meets the international biodiesel standards (EN 14214) specification, with glycerin as a byproduct. The actual process used varies between countries, and the requirements of different export markets. Next-generation biofuel production processes are also being tested in relatively small trial quantities. Palm oil is an edible plant oil derived from the pulp of the fruit of the oil palm (Palm Oil 2010). Thus, the idea to use palm oil as the biodiesel feedstock was not suitable any more as it will create shortage in food supply chain.

2.3.3 Biodiesel from Jatropha Curcas

Jatropha oil is vegetable oil produced from the seeds of the Jatropha curcas, a plant that can grow in marginal lands and common lands. When jatropha seeds are crushed, the resulting jatropha oil can be processed to produce a high-quality biodiesel that can be used in a standard diesel car, while the residue (press cake) can also be processed and used as biomass feedstock to power electricity plants or used as fertilizer (it contains nitrogen, phosphorous and potassium) (Oil, 2010)

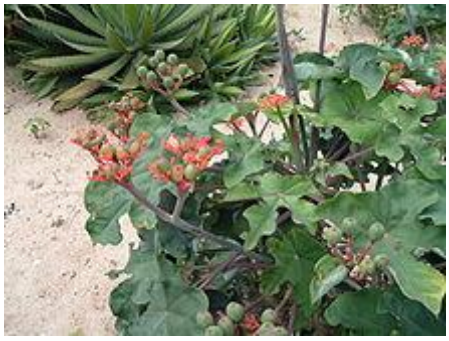

Figure 2.1: Jatropha Curcas

The plant may yield more than four times as much fuel per hectare as soybean, and more than ten times that of maize (corn). A hectare of jatropha has been claimed to produce 1,892 liters of fuel. Goldman Sachs recently cited Jatropha curcas as one of the best candidates for future biodiesel production (Oil, 2010) Jatropha is one of the vegetable oil. However, it is categorized as non-edible vegetable because the seeds and leaves are poisonous. Thus, it will not effecting the food supply chain.

2.4 Transesterification of vegetable oils

As mention in the previous chapter, one of the applications of supercritical condition is the production of biodiesel through the transesterification process. Transesterification means taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acids, removing the glycerin, and creating an alcohol ester. Theoretically, transesterification reaction is an equilibrium reaction. In this reaction, however, more amount of methanol was used to shift the reaction equilibrium to the right side and produce more methyl esters as the proposed product. A catalyst is usually used to improve the reaction rate and yield.

Alcohols are primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms. The alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently. However methanol is preferable because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). Supercritical methanol for biodiesel production was first studied by Saka and his co-workers. This has the advantage of allowing a greater range and water content of feedstock (particularly used cooking oil), the product does not need to be washed to remove catalyst, and is easier to design as a continuous process. In this research, the vegetable oil used is jatropha oil.

The factor lead to this selection is because it is non-edible oil. The leaves and nuts are poisonous. Many research and bio-fuel production widely used palm oil as the feedstock. As mention earlier, Jatropha oil is an alternative way to prevent the shortage in the food supply chain.

Biodiesel, define as fatty acid methyl ester, (FAME), is derived from triglycerides by transesterification of alcohols. The Transesterification reaction proceeds without using primary or secondary monohydric alcohol having 1-8 carbon atoms as follow (Eun-Seok Song, 2007)

Triglycerides + Monohydric alcohol ↔ Fatty Acid Methyl Ester +. Glycerin (2.1)

Excess methanol required in order to shift the equilibrium reaction to the right hence increase the formation of methyl ester. 1 mol of triglycerides reacts with 3 moles of alcohol to produce 3 moles fatty acid methyl ester and 1 mol of glycerin.

1 TG + 3 MeOH ⟷ 3 FAME + 1 GL (2.2)

Biodiesel is made from renewable sources and has become attractive because of its environmental benefit (Hengwen Han, 2005). Biodiesel comes from vegetable or animal fat, making it biodegradable and nontoxic. It has been proven that diesel fuels have viscosities close to those of diesel fuel and has high cetane numbers and flash points (Kalam MA, 2002). It is an alternative for fossil fuels, thus biodiesel becoming an area of high concern.

2.4.1 Catalytic transesterification

The catalyst is dissolved into methanol by vigorous stirring in a small reactor. The oil is transferred into the biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil. The final mixture is stirred vigorously for 2 h at 340 K in ambient pressure. A successful transesterification reaction produces two liquid phases: ester and crude glycerol. Complete settling can take as long as 20 h. Washing the ester is a two-step process, which is carried out with extreme care. A water wash solution at the rate of 28% by volume of oil and g of tannic acid/liter of water is added to the ester and gently agitated. Air is carefully introduced into the aqueous layer while simultaneously stirring very gently. This process is continued until the ester layer becomes clear (Demirbas.A 2005).

2.4.2 Non-catalytic Supercritical Methanol Transesterification

The transesterification of triglycerides by supercritical methanol (SCM), ethanol, propanol and butanol, has proved to be the most promising process. Table 2.2 shows critical temperatures and critical pressures of various alcohols. A non-catalytic biodiesel production route with supercritical methanol has been developed that allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids.

Table 2.2: Critical temperature and critical pressures of various alcohol.

Alcohol	Critical Temperature, (K)	Critical pressure, (MPa)
Methanol	512.2	8.1
Ethanol	516.2	6.4
1-propanol	537.2	5.1
1-butanol	560.2	4.9

A reaction mechanism of vegetable oil in SCM was proposed based on the mechanism developed by Krammer and Vogel for the hydrolysis of esters in sub/supercritical water (Komers.K et al.). The basic idea of supercritical treatment is a relationship between pressure and temperature upon thermophysical properties of the solvent such as dielectric constant, viscosity, specific weight, and polarity (Krammer et al.) The most important variables affecting the methyl ester yield during transesterification reaction are molar ratio of alcohol to vegetable oil and reaction temperature. Viscosities of the methyl esters from the vegetable oils were slightly higher than that of no. 2 diesel fuel.

The variables affecting the ester yield during transesterification reaction are molar ratio of alcohol to vegetable oil, reaction temperature, reaction time, water content and catalyst. It was observed that increasing the reaction temperature, especially to supercritical temperatures, had a favorable influence on ester conversion (Demirbas.A 2002). In the supercritical alcohol transesterification method, the yield of conversion raises 50–95% for the first 10 min. Transesterification reaction of rapeseed oil in SCM has been investigated without using any catalyst. In addition, it was found that this new SCM process requires the shorter reaction time and simpler purification procedure because of the unused catalyst (Demirbas.A 2002).

However, the reaction of methanol and vegetable oil alone are not practicable in the industry. This is because the processes require temperature of 350-400 ^{0}C and

pressures of 45-65 MPa, which are not viable in practice in industry. Besides, that such high temperatures and pressure lead to high production cost and energy consumption. To overcome this problem, additional of co-solvent into this reaction is proposed. A co-solvent was added to the reaction mixture in order to decrease the operating pressure, temperature and molar ratio of alcohol to vegetable oil. With carbon dioxide as co-solvent in the reaction system, there was a significant decrease in the severity of the condition required for supercritical reaction, which make the production of biodiesel using supercritical methanol viable as an industrial process (Hengwen Han, 2005).

The solubility of vegetable oil in methanol increases at a rate of 2 ± 3 % (w/w) per 10^{o}C as the reaction temperature is increased (Ma F, 1998). It is thus of great interest from a practical point of view to investigate the use of the co-solvent, which can increase the mutual solubility of methanol and vegetable oil at low reaction temperature. The variables affecting the methyl ester yield during the transesterification reaction are temperature, pressure, molar ratio of methanol and vegetables oil and molar ratio of methanol and co-solvent.

2.5 Reaction mechanism of transesterification

The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol (Eqs. 8–11). The formation of alkyl esters from monoglycerides is believed as a step which determines the reaction rate, since monoglycerides are the most stable intermediate compound (Ma F, Hanna MA. Biodiesel production: a review. Bioresour Technol 1999;70:1–15).

$$\text{Fatty acid } (R_1COOH) + \text{Alcohol } (ROH) \longleftrightarrow \text{Ester } (R_1COOR) + \text{Water } (H_2O) \quad (2.3)$$

$$\text{Triglycerides} + ROH \longleftrightarrow \text{Diglyceride} + RCOOR_1 \quad (2.4)$$

Diglyceride + ROH $\longleftrightarrow$ Monoglyceride + $RCOOR_2$ (2.5)

Monoglyceride + ROH $\longleftrightarrow$ Glycerol + $RCOOR_3$ (2.6)

When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis.

2.5.1 Non-catalytic Supercritical Reaction Mechanism

A non-catalytic biodiesel production route with supercritical methanol has been developed that allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids. It is evident that at subcritical state of alcohol, reaction rate is very low and gradually increases as either pressure or temperature rises. It was observed that increasing the reaction temperature, especially to supercritical conditions, had a favorable influence on the yield of ester conversion (Demirbas A.2005). In the supercritical alcohol transesterification method, the yield of conversion raises 50–95% for the first 10 min (Demirbas. A 2005).

Water content is an important factor in the conventional catalytic transesterification of vegetable oil. In the conventional transesterification of fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects since the presence of free fatty acids and water causes soap formation consumes catalyst and reduces catalyst effectiveness. In catalyzed methods, the presence of water has negative effects on the yields of methyl esters. However, the presence of water affected positively the formation of methyl esters in supercritical methanol method. Figure 2.2 shows the plots for yields of methyl esters as a function of water content in transesterification of triglycerides. Figure 2.3 shows the plots for yields of methyl esters as a function of free fatty acid content in biodiesel production.